

PATENT
DOCKET 6185US

CERTIFICATION UNDER 37 C.F.R. § 1.10

Express Mail Label No. ET016833404US

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Date of Deposit with Postal Service March 12, 2001

APPLICATION FOR LETTERS PATENT

TITLED:

**GENERATION OF AN ULTRA-SUPERHEATED STEAM
COMPOSITION AND GASIFICATION THEREWITH**

Inventor:

Frederick Michael Lewis

Agent:

Allen H. Erickson
Registration No. 29,792
3493 Dayton Terrace South
Inverness, Florida 34452-7111
Phone/FAX (352) 341-4803
CUSTOMER NO. 25202

**GENERATION OF AN ULTRA-SUPERHEATED STEAM
COMPOSITION AND GASIFICATION THEREWITH**

BACKGROUND OF THE INVENTION

Field of the Invention: This invention relates generally to gasification of carbonaceous materials to useful fuel gases and other products. More particularly, the invention pertains to improvements in generating a highly reactive gasifying agent and customization of carbonaceous compositions, and uses thereof in thermal gasification processes.

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State of the Art:

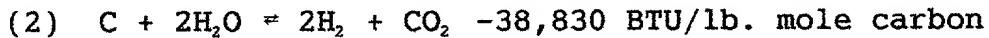
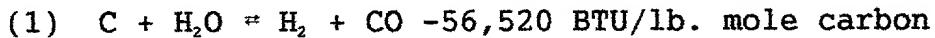
Thermal gasification using superheated steam is a well-known art. In a typical thermal gasification process, a carbonaceous material such as coal or cellulosic waste material is reacted with steam or a hot gas at temperatures greater than about 1400°F (760°C), to produce a combustible fuel gas largely composed of carbon monoxide (CO) and hydrogen (H₂). Carbon dioxide (CO₂) and water vapor (H₂O) are generally present in substantial quantities. Methanation, which increases exponentially with pressure and decreases with reactor temperature, also occurs to produce hydrocarbons e.g. methane. Small amounts of other gases such as ethane and ethylene may also be produced. The gasification conditions are controlled to yield a product gas for use as a fuel or as a feedstock for making

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other hydrocarbon fuels, ammonia, methanol, hydrazine, et.
cetera.

The well-known chemical reactions which occur in thermal
gasification of carbonaceous materials include the following
5 endothermic equations:



The actual composition of the product gas is influenced by
many factors, including the quantities and composition of
10 incoming feed materials, gasification temperature, pressure, and
reactor residence time.

Thus, starting with a set of chemical component input and
gasification conditions, the actual composition of the product
gas is calculated by consideration of reaction rates, chemical
equilibrium, mass balances, and thermal balances. In some
systems, catalysts are utilized to change the reaction rates and
shift the product gas composition.

A major concern in developing workable processes for
gasifying materials such as coal and biosolids is the high
20 thermal energy requirement for driving the endothermic reactions.

In most gasification processes, substantial heat must be
provided to satisfy the highly endothermic chemical reactions.
This heat is typically provided by either (a) partially
combusting the incoming carbonaceous material, (b) exothermically

reacting a material such as calcined lime with carbon dioxide, and/or (c) by providing heat from an outside source, e.g. hot char circulation, addition of excess steam, etc.

In some gasification systems, mixtures of air and steam are used as the gasifying agent, and some of the required heat is provided by oxidation of a portion of the carbonaceous material. In such systems, heating of the inert nitrogen gas in the air wastes energy, and the produced gas will contain a substantial fraction of free nitrogen, resulting in a low heating value.

Gasification with a mixture of steam and pure oxygen has been promoted, but full development has been hindered by (a) the high cost of oxygen, (b) combustion of a large portion of the carbonaceous material to non-fuels (CO_2 and water), and (c) a resulting product gas containing a low ratio of hydrogen gas to the total of carbon dioxide and carbon monoxide. The primary industrial need is for gases with higher $\text{H}_2:\text{CO}$ ratios.

Steam-only gasification has been investigated and used commercially since about 1950-1960. It is usually desirable to maintain a steam:carbon ratio which is close to a value at which the carbon is fully reacted by reactions (1) and (2) above, with minimal excess steam. More particularly, the conversion of carbon to CO should be maximized, as in reaction (1). Thus, an extraneous heat source is usually provided to supply the necessary heating requirements. The product gas typically has a

higher H₂:CO ratio than when gasifying with a mixture of steam and air or oxygen. However, because of the limited heat in the steam, the problems associated with steam-only gasification include low achievable reaction temperatures i.e. typically less than about 1500°F (815°C), where long residence times and high energy consumption prevail. To operate at higher temperatures, complex heat transfer systems are utilized in order to avoid intermingling of combustion gases with the gasification products. Such systems entail high capital and operating costs, and are generally considered to be uneconomic.

In U.S. Patent No. 4,004,896 of Soo, it is proposed to operate a thermal gasification system with a large quantity of excess steam, i.e. 2-10 times that required for full gasification of the carbon. In Soo, the thermal requirements of gasification are provided by copious quantities of steam. However, the quantities of H₂ and CO produced per pound of steam are low.

The use of high temperature superheated steam for gasification processes has been proposed. In a system configuration described in Emerging Technology Bulletin No. EPA/540/F-93/XXX entitled **SPOUTED BED REACTOR**, dated August 1993, by the U.S. Environmental Protection Agency, streams of methane and pure oxygen are fed to a burner, with the hot flame injected into a stream of low temperature steam which is passed into a primary gasification reactor. The gasification temperature is

partially maintained by oxidation of portions of the feed material and gases leaving the reactor. The injected steam supplies only a portion of the heat required to maintain the low gasification temperature.

5 U.S. Patent No. 3,959,401 of Albright et al. describes an apparatus for cracking gaseous and liquid hydrocarbon feedstocks to other chemicals, using a hot gas. It is stated that a hot gas temperature up to 3000°C (5432°F) may be used. The source of the hot gas and its composition is not indicated. Furthermore, the sole purpose of the hot gas is to supply heat for the endothermic cracking reactions. The hot gas does not react to become part of the product. The purpose of the apparatus is cracking, and gasification of carbonaceous materials to CO and H₂ is not in view.

10 In U.S. Patent No. 4,013,428 of Babbitt, an oxygen blown system for gasifying powdered coal is described. A fuel is pre-burned with oxygen to form a mixture of steam and CO₂, to which a small amount of water is added. The combustion temperature is indicated to be about 4722°F, and the gas is contacted with the 20 powdered coal to produce a product gas. Each of fuel, oxygen and steam is separately introduced into the pre-burner.

Babbitt also describes a process in which the pre-burner is fed separate streams of fuel, air and steam, creating a gasifying agent containing CO₂, steam and inert nitrogen at a temperature

of about 3770°F. The presence of nitrogen is detrimental to energy efficiency and results in a product gas of lower heating value.

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BRIEF SUMMARY OF THE INVENTION

A primary object of the present invention is to provide a gasification process for gasifying a carbonaceous material such that a maximum quantity of usable product gas is obtained per unit of steam introduced into the gasifier reactor.

Another object of the invention is to provide a thermal gasification process in which a maximum quantity of usable product gas is obtained per unit of oxygen burned in a pre-burner, in order to operate at lower cost.

A further object of the invention is to provide a thermal gasification process in which both water vapor and carbon dioxide in the product gas are substantially reduced.

Another object of the invention is to provide a gasification process in which the gasification rate at temperatures of about 1200°F (649°C) to about 2200°F (1204°C) is significantly increased.

An additional object of the present invention is to provide a gasification process in which the gasifying agent is a high energy ultra-superheated steam composition substantially free of oxygen and nitrogen, and contains a high concentration of

dissociation free radicals.

A further object of the invention is to provide a gasification process wherein all or nearly all of the heat requirement is supplied by the gasifying agent.

5 Another object of the invention is to provide methods for maximizing the concentrations of CO and H₂ in the product gas.

An additional object of the invention is to provide methods for controlling a gasification system at conditions optimal with respect to raw material consumption, yield, and cost.

10 Other objects and considerations of the invention will become apparent in the description of the invention when taken in conjunction with the attached drawings.

In accordance with the invention, it has been discovered that a highly reactive composition of steam may be formed under certain conditions. This composition is denoted herein as ultra-superheated steam, abbreviated as USS, and is indicated as providing significant advantages as a gasifying agent in thermal gasification of carbonaceous materials including elemental carbon, hydrocarbons, cellulose, etc.

20 In its most reactive or "pure" form, ultra-superheated steam comprises a mixture of water vapor and carbon dioxide, together with an enhanced population of free radicals of the combustion products, and is formed under such conditions that it is substantially devoid of free oxygen and free nitrogen. Moreover,

the temperature of USS is defined as being significantly greater than steam produced in even the most advanced existing steam generating power plants, i.e. greater than about 2400°F (1316°C). As described herein, USS may be produced at temperatures ranging 5 from about 2400°F (1316°C) to about 5000°F (2760°C).

In order to produce USS, a substantially ash-free carbonaceous fuel such as fuel oil, natural gas, etc. is burned by a homogeneous mixture of oxygen and water vapor at or very near to stoichiometric fuel:oxygen conditions. It has been found that the oxygen and water vapor must be homogeneously mixed prior to contact with the fuel. In practice, either the oxygen or water vapor, or the mixture thereof, may be preheated depending upon the heating value of the fuel and system parameters.

It has been discovered that when the stoichiometric combustion is conducted in a high-turbulence burner such as one having an aerodynamic or bluff body flame holder, at an adiabatic stable flame temperature of about 2400°F (1316°C) to about 5000°F (2760°C), a USS composition is produced as a distinctive clear, colorless flame indicative of a high concentration of free radicals. These free radicals are known to generally enhance reaction rates and reaction completion. 20

In another aspect of the invention, it has been discovered that the chemical and thermodynamic efficiencies of gasification may be significantly increased by gasifying certain mixtures of a

carbonaceous material containing little or no oxygen with a carbonaceous material containing oxygen. This gain of CO and H₂ may occur at both ends of the composition spectrum. For example, supplementing an α -cellulose material with up to about 30-40 w/w % elemental carbon, or supplementing an elemental carbon material with up to about 5-8 w/w % α -cellulosic material enhances burnable gas production per unit of oxygen consumed. Moreover, the "cold efficiency" of the process, defined as the chemical heat in the product gas divided by the total heat input, is increased by reducing the CO₂ and free water vapor. The heating value of the produced gas is increased by reducing the CO₂. Although a similar heating value increase is achieved by the reduction of H₂O, the product gas is generally dried prior to use. An optimal ratio of carbon and cellulosic material may be maintained by controlling the feed material ratio to maintain a CO₂ or water content of the gasification reactor outlet gas at a low value approaching zero. Use of a mixed feed material permits control of a gasification process to produce a particular composition of product gas.

The utilization of each of these aspects in combination results in a very rapid gasification with low oxygen consumption, low steam consumption, and a high heating value product gas, e.g. "syngas".

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated in the following figures,
wherein:

FIG. 1 is a generalized block diagram of a gasification
process in accordance with the invention;

FIG. 2 is a general cross-sectional side view of a high
turbulence burner which is representative of burners useful in
the practice of the invention;

FIG. 3 is a graphical depiction of produced gas composition
at 2000°F for gasification by 4000°F ultra-superheated steam of
elemental carbon supplemented with pure α -cellulose in accordance
with the invention;

FIG. 4 is a graphical depiction of the net chemical heat
output per pound of burner oxygen consumed to produce a 4000°F
ultra-superheated steam in a 2000°F gasification process in which
elemental carbon is supplemented with pure α -cellulose in
accordance with the invention;

FIG. 5 is a graphical depiction of produced gas composition
at 2000°F for gasification by 4000°F ultra-superheated steam of
pure α -cellulose supplemented with elemental carbon in accordance
with the invention;

FIG. 6 is a graphical depiction of the net chemical heat
output per pound of burner oxygen consumed to produce a 4000°F
ultra-superheated steam in a 2000°F gasification process in which

pure α -cellulose is supplemented with elemental carbon in accordance with the invention;

FIG. 7 is a graphical depiction of produced gas composition at 2000°F for gasification by 3000°F ultra-superheated steam of an elemental carbon material supplemented with pure α -cellulose in accordance with the invention;
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FIG. 8 is a graphical depiction of the net chemical heat output per pound of burner oxygen consumed to produce a 3000°F ultra-superheated steam in a 2000°F gasification process in which an elemental carbon material is supplemented with pure α -cellulose in accordance with the invention; and
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FIG. 9 is a generalized diagram of an exemplary gasification system for illustrating the practice of various aspects of the invention.
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DESCRIPTION OF THE PREFERRED EMBODIMENTS

In this discussion, the term "ultra-superheated steam" or simply "USS" denotes a "synthetic" steam mixture whose composition is substantially water vapor (H_2O) and carbon dioxide (CO₂), together with a high concentration of their free radical dissociation products. As defined herein, pure USS is substantially devoid of oxygen (O₂) and contains little or no nitrogen gas. It is difficult to produce USS which has absolutely no trace of nitrogen or oxygen, and such is not
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generally needed for most gasification applications. Thus, in the methods of the invention, the term USS refers to a steam composition which may contain up to about 3.0 molar percent oxygen and/or up to about 10.0 molar percent nitrogen.

5 For the purposes of this invention, USS is produced at a minimum temperature of about 2400°F (1,316°C, 1589°K), but may have a temperature up to about 5000°F (2760°C). Under the conditions at which USS is formed, the equilibrium between CO and CO₂ highly favors CO₂.

10 In accordance with this invention, USS is produced by combining the following conditions:

(1) An "artificial air" is formed by combining an enhanced oxygen gas and water vapor. The oxygen content of the enhanced oxygen gas is at least about 80 molar percent, and preferably at least about 90 molar percent, and the artificial air may have an oxygen content of between about 15 molar percent and about 40 molar percent.

(2) A substantially ash-free fuel such as methane, natural gas, fuel oil, etc. is burned with the "artificial air".

20 (3) The oxygen provided by the "artificial air" is controlled to be essentially stoichiometric with respect to the ash-free fuel, so that very little free oxygen remains upon combustion.

(4) The oxygen and water vapor of the "artificial air" must be well mixed prior to contact with the fuel in a burner.

(5) The combustion of fuel with the artificial air takes place in a high turbulence burner with an aerodynamic or bluff body flame holder at an adiabatic flame temperature of about 2400°F (1316°C) to about 5000°F (2760°C).

5 Production of ultra-superheated steam at these high flame temperatures is characterized by a clear colorless "flame" in the burner flame holder, complete oxidation of the fuel, and a complete absence of soot. Clear colorless flames are characteristic of the generation of large quantities of dissociation products, i.e. high energy free radicals. When an oxygen-free USS is injected into a gasification reactor, no exothermic reactions will occur outside of the flame envelope.

10 Before proceeding further, it is necessary to define several terms used in this description. The term "substantially ash-free" refers to a fuel such as commercially available natural gas, propane, fuel oil, etc.

15 The term "carbonaceous" will be used herein to define a fuel or gasifiable material which contains elemental carbon, carbohydrate or hydrocarbon materials. Such materials may occur naturally or may be man-made, and may be solid, liquid or gas at ambient temperatures. Carbonaceous materials which are commonly gasified on a large scale include coal, cellulosic materials (biomass), hydrocarbon fuels and the like.

20 The term "flame temperature" is used herein to denote a

calculated temperature of the combustion flame based on thermodynamic considerations. Actual accurate measurement of a flame temperature is very difficult. Thus, a theoretical adiabatic flame temperature is determined by calculation, 5 ignoring any heat losses by radiation or other means to the atmosphere. Likewise, energy conversion in forming free radicals is ignored in the flame temperature calculations, since the effect is difficult to quantify.

The term "chemical heat" will be used to define the heat of combustion present in a fuel such as natural gas, coal or product gas (syngas).

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Turning now to FIG. 1, the steps in a gasification method 10 using USS 40 are depicted. As shown, an oxygen enriched gas 14 containing at least about 80 percent oxygen, and preferably at least about 90 percent oxygen, is mixed in pre-mix step 20 with water vapor 18 to form an "artificial air" 30. The oxygen may comprise anywhere from about 15 mole percent to about 40 mole percent of the artificial air 30. The pre-mixing of the oxygen enriched gas 14 and water vapor 18 is important to ensure a uniform blend thereof before introduction into the combustion step 36. In actual practice, the water vapor 18 may be provided as low pressure steam. The term "artificial air" was coined because when pure oxygen is bubbled through water at a temperature of 200 °F (93.3°C) at atmospheric pressure, the

resulting gas mixture at equilibrium will contain about 21 percent oxygen, similar to air. The nitrogen content of air is replaced by water vapor to avoid the addition of inerts to the gasifier 44. The "artificial air" 30 may be preheated in step 22 by heat input 26, and is passed to a combustion step 36 as heated artificial air stream 32 to intimately contact and oxidize a substantially ash-free fuel 34. Some or all of the heat input 26 may be provided by heat exchange with the hot product gas 52 from the gasification process 44.

The formation of a high energy USS composition 40 in combustion step 36 appears to depend upon an efficient, stable, high turbulent combustion of the fuel 34 and artificial air 32. There may be many types of burner constructions which will meet these requirements. Examples of such include burners are those in which the combustion takes place entirely within the flame stabilization zone 28A within an aerodynamic or bluff body flame holder 28 of the burner 38, a particular example of which is generally depicted in FIG. 2. Use of such burners 38 to provide USS composition 40 to a gasifier 44 avoids the requirement for expensive complex equipment for avoiding the contact of burner oxygen 14 with the gasifier feed material 42, and oxidation thereof.

Many of the burners 38 which may be used are commercially available for operation at temperatures up to about 5000°F

(2760°C) and higher. Examples of such burners 38, without limitation thereto, are those designed for use with air pre-heated to a temperature of approximately 1,300°F (704°C) and those designed for use with oxygen-enriched air, i.e. >21% 5 oxygen. Some available burners have a construction which inherently mixes the oxidizing gas prior to combustion.

Returning to FIG. 1, the combustion step 36 produces an ultra-superheated steam 40 at a controllable adiabatic flame temperature of about 2400°F (1316°C) to 5000°F (2760°C). As already noted, this USS composition 40 comprises primarily water vapor, carbon dioxide and dissociation products thereof, i.e. free radicals. The free oxygen in the USS composition 40 is very low, e.g. typically less than about 3 molar percent. The USS composition 40 may contain a small quantity of nitrogen gas, depending upon the oxygen purity of the enriched gas 14.

As shown in FIG. 1, the ultra-superheated steam composition 40 may be directed to a gasification process 44, where it comprises the gasifying agent. Given a constant feed rate of carbonaceous feed material 42 to the gasifier 44, the 20 gasification temperature, i.e. temperature of outlet product gas 52, is maintained by controlling both the temperature and quantity of USS composition 40. The USS composition temperature is controlled by varying the ratio of water vapor 18 to either fuel 34 or oxygen enriched gas 14. The quantity of USS

composition 40 per unit feed material 42 is varied to provide the required energy for maintaining the desired temperature.

As is well known, gasification of feed materials 42 such as coal, common waste materials and the like results in formation of inert ash 46, which is discharged from the gasification process 5 44.

Several advantages of the use of USS composition 40 in thermal gasification process 44 result in part from the substantial exclusion of oxygen and nitrogen. The endothermic gasification reactions may be controlled to generate product gases 52 largely containing carbon monoxide and hydrogen. If the gasifier reaction takes place at high pressure, the equilibrium shifts toward the production of methane or other hydrocarbons. In either case, use of USS composition 40 results in very rapid gasification and complete conversion of the carbonaceous feed material 42. The water vapor and CO₂ are substantially all converted to H₂ and CO, with little CO₂ remaining in the gasifier product gas 52. The quantity of oxygen 14 required to be consumed in burner 38 is relatively low, resulting in 20 improvements in gasification efficiency. Thus, the high cost of oxygen and complex equipment may be ameliorated in this process which uses much less oxygen, avoids the introduction of inert materials, e.g. N₂, achieves very high gasification rates, avoids the requirement for large excess quantities of expensive steam,

and uses conventional off-the-shelf apparatus.

With an ultra-superheated steam composition 40, all of the heat required to achieve the desired gasification temperatures may be provided by the change in sensible enthalpy of the USS, i.e. none of the gasification feed material 42 need be burned. This may be achieved by operating the combustion process 36 at a high adiabatic flame temperature which is controlled to provide the necessary heat. In actual practice, a portion of the energy in the product gas 52 is recovered in a superheater and waste heat boiler to heat the incoming artificial air 32.

Furthermore, because of the high (but unquantified) concentration of highly reactive free radicals in USS compositions 40, the endothermic gasification reactions are believed to be accelerated. Thus, a very rapid and efficient gasification process results from operation at stoichiometric or near-stoichiometric steam addition, without providing additional heat by other means.

Turning now to FIG. 9, an exemplary gasification system 10A illustrates various aspects of the invention. Gasification reactor 48 is shown with a high turbulence burner 38 having a flame stabilization zone 28A in a flame holder 28 (see FIG. 2).

The burner 38 is fed a substantially ash-free fuel 34 such as methane, propane, natural gas, gasification product gas or a liquid fuel such as fuel oil. A homogeneous mixture of oxygen 14

from oxygen source 12 and water vapor 18 from waste heat boiler 16 is heated as artificial air stream 30 by passage through superheater 54. The heated artificial air 32 is injected into burner 38 where it is mixed with fuel 34 and burned under turbulent conditions, creating a ultra-superheated steam (USS) composition 40 having an adiabatic flame temperature of between about 2400°F (1316°C) to 5000°F (2760°C). In the gasification reactor 48, a carbonaceous feed material 42 is gasified by the USS composition 40 at a temperature of about 1200°F (649°C) to about 2200°F (1204°C). The product gas 52 is cooled in superheater 54 and passes as cooled product gas 56 to waste heat boiler 16 for heating boiler feed water 58. The heated boiler feed water 58 is typically heated to become a saturated steam 18 which is homogeneously mixed with oxygen 14 to become "artificial air" 30.

In this example, the further cooled product gas 60 is then scrubbed by a water stream 64 in scrubber 62. The scrubbed cooled product gas 68 is then dried in dryer 70. Wastewater streams 66 and 72 are shown in the figure. The dry product gas 50 is then available for export from the system 10A. Optionally, a portion 50A of the dry product gas 50 may comprise a portion or all of the fuel 34 introduced into the burner 38. A portion or all of the recycled portion 50A may comprise wet product gas 74, which thus supplies water vapor to the burner 38.

In another aspect of the invention, depicted in FIGS. 3-8, it has been discovered that the feed material to be gasified may comprise a mixture of different materials, and the contribution of each component material controlled to enhance the overall 5 gasification efficiency. The carbonaceous materials which are normally gasified generally fall into two classes. The first class is a material whose carbon content substantially comprises elemental carbon, such as coal for example. The second class is a carbonaceous material which contains a substantial percentage of oxygen, typically molecularly bound. Examples of such materials are cellulose or various hydrocarbons.

It has been discovered that, for example, a relatively minor addition of coal having no or little combined oxygen to a cellulose material having a relatively large combined oxygen content results in a produced gas of enhanced CO and H₂, and the yield per unit of oxygen consumed in the burner may be maximized. Furthermore, yield and composition enhancement also occur when a minor amount of cellulose material is added to a coal.

Thus, as shown in FIG. 9, the gasifier feed material 42 may 20 comprise a low oxygen material 42A such as coal, and an oxygen-containing material 42B such as α -cellulose. A commonly used chemical formula for α -cellulose is C₆H₁₀O₅, which indicates that it contains nearly 50 w/w percent oxygen.

Depending upon the particular type and characteristics of

the materials to be gasified, as well as gasification conditions, it may be generalized that in one embodiment of the invention, the low oxygen carbonaceous material 42A such as coal may comprise about 5 w/w % to about 50 w/w % of the total feed material 42.

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In another embodiment, the carbonaceous material 42B containing substantial oxygen may comprise about 5 w/w % to about 25 w/w % of the total feed material 42.

The curves of FIGS. 3-8 were developed by simultaneously solving for the gas components integrating known equilibria relationships into mass and energy balances. In FIGS. 3, 5 and 7, the mole percentage 76, 78, 80, 82 and 84, respectively of each gas component CO, CO₂, H₂, H₂O and CH₄ is plotted as a function of the weight percentage of elemental carbon 42A or cellulose 42B in the gasifier feed material 42. In FIGS. 4, 6 and 8, the net gain in chemical heat, i.e. product gas BTU minus feed material BTU, times 1000, per pounds of oxygen 14 consumed in the burner 48, is plotted as a function of the feed material composition.

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In FIGS. 3 through 6, the temperatures of the burner 38 and reactor outlet gas 52 are assumed to be 4000°F and 2000°F, respectively. In FIGS. 3 and 4, a small quantity of an elemental carbon material 42A, e.g. coal is added to a cellulose material 42B as the input material 42 to a gasifier 48. As the weight percentage of carbon 42A in the mixture 42 increases from

zero to about 38 percent, the CO content 76 and H₂ content 80 of the product gas 52 increases. Simultaneously, the CO₂ 78 content and H₂O content 82 fall to zero. Thus, to operate at the most efficient condition, the produced gas 52 may be analyzed for CO₂ or H₂O, and the feed mixture 42 adjusted to control the mole percentage of the particular analyzed gas (CO₂ or H₂O) at a positive value near zero, at 3-5 mole percent for example. FIG. 5 shows that the net chemical heat output increases many times over as the content of carbon 42A is increased. Thus, for example, the addition of about 35 w/w percent carbon 42A to a gasification feed material comprising cellulose material 42B increases the net chemical heat per pound of oxygen consumed in the burner by about 800 percent. Moreover, calculations indicate that the CO content 76 and H₂ content 80 in the product gas 52 are significantly increased.

Likewise, a similar phenomenon occurs at the other end of the composition spectrum. As depicted in FIGS. 5 and 6, a small quantity of cellulose material 42B is added to a gasification feed material comprising carbon 42A e.g. coal feed material. The indicated peak of enhanced efficiency is shown to occur at about 20 7 percent cellulose 42B (93 percent carbon 42A). Thus, gasifier operation may be optimized by operating with a feed material 42 containing about 6 percent cellulose (94 percent carbon), which results are achieved for example by controlling the product gas

CO₂ mole percent 78 at about 3-5 percent.

In either case, the gasifier 48 may be controlled at near-ideal conditions by monitoring the produced gas composition produced in the gasification reactor. The fraction of interest which is monitored may be either the CO₂ fraction or the water vapor fraction. The carbon:cellulose composition of the feed material 42 is then controlled to maintain the CO₂ or water vapor content at the reactor outlet at a selected controllable positive value approaching zero, e.g. 1-5%.

Using USS composition 40 of a higher temperature, the quantity of USS used may be decreased while yet supplying the required heat to drive the gasification reactions.

FIGS. 7 and 8 are analogous to FIGS. 5 and 6, depicting the product gas composition and net chemical heat output when the burner flame temperature (USS temperature) is reduced to 3000°F. A similar pattern of composition and net heat output are evident, but the CO₂ concentration 78 and H₂O concentration 82 drop to zero at a somewhat lower mole concentration (about 90.5%) of carbon 42A in the feed material 42. The net chemical heat output per pound oxygen consumed is greatly increased by adding 8-9 percent cellulosic material 42B to the elemental carbon material 42A.

Thus, the gasification process may be controlled to maximize the CO and H₂ content. The production of CH₄ and higher order

hydrocarbons increases exponentially with pressure and decreasing reactor temperature.

Example A

5 Experiments in producing USS were conducted using a commercially available burner produced by North American Manufacturing Company of Cleveland, Ohio. The burner, identified as a model #4425-3, with a nominal rating of 350,000 BTU/Hr., has an aerodynamic flame holder for producing a stable flame under high turbulence conditions. The burner was mounted on a test stand in the Enercon Systems factory in Elyria, Ohio, and directed to fire through a hole through the factory wall to the outside. A sheet metal tube was placed about one foot away from the burner flame to shield the flame from direct sunlight for personal observation. Additional cooling air was allowed to enter the duct coaxially to avoid overheating the duct.

10 The oxidizing gas fed to the burner was either (1) air, or (2) a "synthetic air" comprising a mixture of oxygen (21% w/w) and steam (79% w/w), and the fuel comprised natural gas having a heating value of about 1,000 BTU per cubic foot (7140 Kcal per 20 cubic meter). The oxidizing gas pressure was approximately 1 psig. The water vapor i.e. steam was generated by a very small boiler with manual control of the natural gas flow rate to produce water vapor at about 215°F (102°C). The boiler was

operated at less than 10 psig pressure. The burner ignition pilot of the boiler was operated with a conventional air/natural gas mixture to avoid unnecessary experimental problems. The quantity of nitrogen introduced by the pilot air was calculated to be less than about 0.1 percent of the high temperature ultra-superheated steam (USS) 52 which was produced. The flow rates of oxygen, steam and natural gas flows were measured by orifice plates.

The operating conditions and results were as follows:

Ambient Air Test

Air composition: 79 w/w % nitrogen, 21 w/w % oxygen

Firing Rate: approximately 300,000 BTU/Hr.

When observed during operation with ambient air as the oxidizing gas, the burner produced a blue flame with yellow and red tinges on the flame tips; this observation is normal for combustion with air. The calculated adiabatic flame temperature under these conditions was 3550°F (1954°C).

Artificial Air Test

Artificial Air Composition:

21 w/w % oxygen

79 w/w % water vapor

Firing Rate: Approximately 300,000 BTU/Hr.

During operation with the "synthetic air", the flame was observed to be clear and colorless, i.e. invisible. However, the

sheet metal ducting was very hot i.e. glowing red, and the invisible "flame" was radiating a great deal of heat. The calculated adiabatic flame temperature under these conditions was 3270°F (1799°C). As is well known, a clear, colorless flame is 5 indicative of the presence of large numbers of free radicals which enhance reaction rates.

Contrary to expectations, the "synthetic air" established and maintained a stable flame with no problems whatsoever.

Example B

Heat balances and material balances about a thermal gasification system of FIG. 9 were calculated using a computer program for simultaneously solving for steady state equilibrium conditions with mass and energy balances. The assumed operating conditions are:

The rate of carbonaceous feed material 42 to reactor 48 is set at 1.00 ton per hour.

The mixture of gasifier reactor feed material 42 comprised:

	<u>w/w Percent</u>	<u>lb./hour</u>	<u>Heat Value, BTU/pound</u>
20	Elemental Carbon 35.00%	700 lb.	14,100
	Cellulose 65.00%	1300 lb.	7,500
	Total 100.00%	2000 lb.	(ave. 9,810)

This mixture was chosen from the curve of FIG. 5, which indicates improved performance at this feed mixture 42. Pure

elemental carbon and pure cellulose of composition $C_6H_{10}O_5$ were assumed.

It was assumed that burner fuel 34 comprises methane of heating value 1000 BTU/cubic foot.

5 Pre-mixed and pre-heated artificial air 32 is assumed to be at a temperature of 1200°F (649°C), and comprises 79.30 w/w % water vapor 18 and 20.70 w/w % oxygen 14. The oxygen 14 is stoichiometric with respect to burner fuel 34.

Artificial Air

Steam 18	22.98 moles	413.95 lb.
Methane 34	3.00 moles	48.10 lb.
Oxygen 14	6.00 moles	191.90 lb.
Total	31.97 moles	653.94 lb.

Reactor Pressure: approximately atmospheric

Gasifying Agent: The burner 38 at the above conditions produces a USS composition 40 at 4000°F (2204°C) comprising the following:

Steam portion	28.97 moles	521.98 lb.
CO ₂	3.00 moles	131.96 lb.
Total	31.97 moles	653.94 lb.

<u>Burner Inlet:</u>	<u>Heat Input, BTU/Hr.</u>	<u>Percent of Total</u>
Steam, Heat of Vapor.	433,980	22.61
Steam, Sensible Heat	226,431	11.79

Oxygen, Sensible Heat 111,014 5.78

Methane, Chemical Heat 1,148,380 59.82

Total 1,919,805 100.00

Burner Outlet: Heat Output, BTU/Hr. Percent of Total

5 Steam, Heat of Vapor. 547,246 28.51

Steam, Sensible Heat 1,217,195 63.40

CO₂, Sensible Heat 155,364 8.09

Total 1,919,805 100.00

Gasification Outlet Temperature: 2000°F (1093°C).

The material and heat balances for the gasification reactor

48 are as follows:

Overall Material Balance:

<u>Material In</u>	<u>Moles</u>	<u>Pounds</u>
Carbon	80.56	967.49
Hydrogen	88.28	177.98
Oxygen	<u>47.14</u>	<u>1508.47</u>
Total	215.98	2653.94

<u>Material Out</u>	<u>Moles</u>	<u>Pounds</u>
CH ₄	0.47	7.59
CO ₂	8.99	395.57
CO	71.10	1991.38
H ₂ O	5.21	93.82

H ₂	<u>82.13</u>	<u>165.57</u>
Total	167.89	2653.94

The composition of the product gas 52 from the
5 gasification reactor 48 is as follows:

<u>Component</u>	<u>Mole %</u>	<u>Weight %</u>	<u>Dry Basis, mole %</u>
CH ₄	0.28	0.29	0.29
O ₂	5.35	14.91	5.52
CO	42.35	75.04	43.70
H ₂ O	3.10	3.54	0.00
H ₂	<u>48.92</u>	<u>6.24</u>	<u>50.48</u>
Total	100.00	100.00	100.00

The heat input to the gasifier reactor 48 is as follows:

<u>Component</u>	<u>BTU/hour</u>
From burner gases	1,919,805
From reacting solids	<u>19,620,000</u>
Total	21,539,805

The heat output from the reactor 48 is as follows:

20	<u>Component</u>	<u>BTU/hour</u>	<u>% of total</u>
	Chemical Heat in CH ₄	181,246	0.84
	Chemical Heat in H ₂	10,116,441	46.97
	Chemical Heat in CO	8,656,547	40.19
	Heat of Vaporiz., H ₂ O	98,358	0.46

Sensible Heat in CH ₄	14,015	0.07
Sensible Heat in CO ₂	208,839	0.97
Sensible Heat in CO	1,045,352	4.85
Sensible Heat in H ₂ O	94,167	0.44
5 Sensible Heat in H ₂	<u>1,124,839</u>	<u>5.22</u>
Total	21,539,805	100.00

Various indicators of the process efficiencies are as follows:

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100

- (a) Pounds of reacted material 42 per 1000 pounds of steam = 4831.56.
- (b) Pounds of reacted material 42 per pound of oxygen consumed= 10.422.
- (c) Chemical BTU's generated per pound of oxygen = 98,774.
- (d) (Output chemical heat-Input chemical heat)/pound oxygen=92,790.
- (e) Pounds methane used per ton of material 42 gasified= 48.10.
- (f) Ratio of chemical heat output to methane input= 16.51.
- (g) (Total heat from steam and oxygen)/(heat from methane)=0.67.
- (h) Calculated COLD efficiency= 88.00%.
- (i) Calculated High Heating Value (HHV) of produced gas, BTU per cubic foot (dry) = 307
- (j) Total BTU/hour Chemical Heat = 18,954,235.
- (k) Initial Chemical Heat/Final Chemical Heat = 6.06 percent.

(1) (Initial Chemical Heat + Heat of Vaporization)/ Final
Chemical Heat = 8.35 percent.

It should be noted that in this analysis, product gas 52 is cooled in superheater 54 from 2000°F (1093°C) to 1858°F (1014°C), while incoming artificial air 30 is heated to 1200°F (649°C). In 5 the waste heat boiler 16, feedwater 58 is heated from 80°F (27°C) to become saturated steam at 250°F (121°C), while the partially cooled product gas 56 is cooled from 1858°F (1014°C) to 1359.3°F (737.4°C).

The operating cost for this example may be calculated from the following assumed costs:

Boiler water	\$ 0.08 per gallon (\$1.28/1000 lbs.)
Methane	10.00 per million BTU
Carbon (coal)	40.00 per ton (\$1.42 per million BTU)
Cellulose	\$ 20.00 per ton (\$1.33 per million BTU)

Based on these assumptions, the net materials cost for this gasification example is \$2.27 per million BTU in the produced gas. The breakdown indicates that the cost of oxygen is reduced 20 in this gasification process to less than 9 percent of the total:

Cost of Boiler water (steam)	1.56%
Cost of Methane	26.71%
Cost of Oxygen	8.93%
Cost of Carbon (coal)	32.57%

Cost of Cellulose	<u>30.24%</u>
Total Materials Cost	100.00%

The several examples of producing and using ultra-
5 superheated steam which are shown and described herein are
considered to be exemplary only, and the descriptions of
operating conditions and apparatus utilized thereon are not to be
interpreted as limiting the invention.

Thus, it is apparent to those skilled in the art that
various changes and modifications may be made in the methods and
apparatus of the invention as disclosed herein without departing
from the spirit and scope of the invention as defined in the
following claims.

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